BAKERIAN LECTURE:—*On the Variation of the Specific Heat of Water, with Experiments by a New Method.*

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(Abstract.)

The question of the variation of the specific heat of water is so fundamental in calorimetry, and the results of different observers and different methods are still so discordant, that no apology is needed for the publication of fresh experimental evidence. The continuous electric method, which I carried out in conjunction with Prof. Barnes,* was specially designed to avoid the main sources of error of the older methods in which mercury thermometers and open calorimeters were employed. In this method, the rise of temperature of a steady current of water, heated by a steady electric current in its passage through a fine tube hermetically sealed in a vacuum-jacket, was observed with a differential pair of platinum thermometers. Errors due to lag, or to uncertainty of water-equivalent, or to evaporation or heat-loss in transference, were thus eliminated, and a higher order of accuracy was secured in the temperature measurements.

The results of the continuous electric method in the case of water showed a variation of specific heat amounting to less than one half of 1 per cent. between 10° and 80° C., with a minimum at 37·6° C., followed by a very slow and steady rise. The mean value from 0° to 100° C. agreed to 1 in 2000 with the experiments of Reynolds and Moorby by the mechanical method, and the values from 5° to 35° C. agreed to a similar order of accuracy with the experiments of Rowland. But the value at 80° C. was 1 per cent. lower than that found by Lüdin (Zürich, 1895), employing the ordinary method of mixture with an open calorimeter and mercury thermometers. Lüdin's results for the variation over the range 30° to 100° C. agreed more closely with the continuous electric method than those of any previous observers; but showed a minimum at 25° C., and a maximum at 87° C., which could not be reconciled with the experiments of Reynolds and Moorby on the mean specific heat from 0° to 100° C., or with the most probable reduction of Regnault's experiments between 110° and 190° C.

Within the last year the results of Lüdin have been almost exactly repro-

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* Callendar and Barnes, 'Phil. Trans.,' A, 1902, vol. 199, pp. 55–263.

duced by W. R. and W. E. Bousfield,* employing a Dewar calorimeter electrically heated by a mercury resistance. The mouth of the calorimeter was partially closed by an "obturator," maintained at a temperature 10° above that of the calorimeter, in order to minimise heat-loss due to evaporation, etc. The rise of temperature of the water in the calorimeter due to a measured supply of electrical energy was observed with mercury thermometers standardised to 0·01° every 5° C. Their results, like Lüdin's, showed a minimum at 25° C., and a maximum at 80° C., exceeding the value given by the continuous electric method by nearly 1 per cent. They attribute the discrepancy partly to uncertainty of the absolute value of the Clark cell in 1902, and partly to some heating effect of the current on the platinum-silver standard employed for the current measurement in the continuous electric method. In reply it may be urged that: (1) In default of satisfactory standards of comparison, the absolute value of the type of Clark cell employed was determined by direct experiment with a specially designed electrodynamometer by myself and Mr. King in 1898, and has since been verified to 1 in 14,000 by the independent evidence of Woolf and Waters.† (2) The platinum-silver standard was designed to carry 32 watts for a rise of temperature of 1° C. in a well-stirred oil-bath. Messrs. Glazebrook, Bousfield, and Smith, from their recent experiments,‡ are able to estimate the rise of temperature of this particular coil, under these conditions, as 0·95°, which agrees very well with my own experiments on which the design of the coil was based. Under the actual conditions of use, when carrying 20 watts as a maximum, the rise would probably not have exceeded 0·6° C., giving an increase of less than 1 in 5000 in the resistance, which was within the limits of error of the absolute determinations. (3) Uncertainty of the electrical measurements, if it existed, could not, in any case, explain the large discrepancy in the variation of the specific heat at 80° C., because the relative values of the specific heat were practically independent of the absolute values of the standards employed.

Assuming on the above grounds that the discrepancy must be due to some fundamental difference in the calorimetric and thermometric methods, it appeared desirable to verify the variation of the specific heat in the neighbourhood of 80° C., by an independent method. The "continuous mixture method," which I had already designed for experiments at higher temperatures, appeared peculiarly suited for the purpose, and was applied as follows to the question at issue. A steady current of air-free water at a measured temperature t_1 in the neighbourhood of 100° C., is passed through an arrangement of concentric tubes, called a "heat exchanger" (as indicated in the flow diagram annexed), where it loses some of its heat, emerging at a measured temperature, t_2, in the neighbourhood of 70° C. The current is then cooled to an accurately regulated temperature t_3, in the neighbourhood of 30° C., and is passed through the heat exchanger again as a cold current, abstracting heat from the hot current by conduction, without actual mixture, and emerging at a measured temperature, t_4, in the neighbourhood of 60° C. By a suitable arrangement of the flow tubes, the external heat-loss can be reduced almost to a vanishing quantity, without the employment of vacuum-jackets or elaborate precautions in lagging. The flow can be varied over a very wide range (20 to 1) without materially affecting the distribution of temperature; and, since the hot and cold currents are the same, a comparatively rough measurement of the current suffices for the determination of the heat-loss. The water equivalent of the exchanger is immaterial, provided that the conditions are steady, and there is no possibility of uncertain loss by evaporation, as in the case of an open calorimeter. The accuracy attainable is limited chiefly by the temperature readings, which were taken with platinum thermometers to 0·001° C., equivalent to 1 in 30,000 of the heat-exchange. Since the loss of heat by the hot current is equal to the gain of heat by the cold current, *plus* the small external heat-loss, the experiment gives the ratio of the mean specific heat from t_2 to t_1 (70°—100°) to the mean specific heat from t_3 to t_4 (30°—60° C.).

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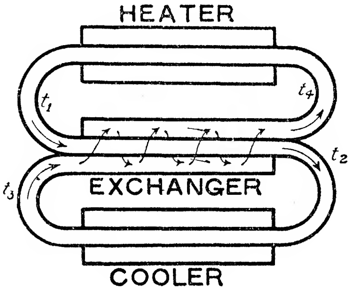
* 'Phil. Trans.,' A, 211, pp. 199–251.

† 'Bull. Amer. Bur. Stan.,' 1907.

‡ 'Roy. Soc. Proc.,' September, 1911.



The results of about 150 experiments by this method, in which the conditions as to flow and heat-loss were varied as widely as possible, were such as to confirm the continuous electric method over this range of temperature to less than 1 in 5000, whereas they differed from Lüdin's formula by more than 1 in 200.

An expression of the ordinary type $1 + at + bt^2 + ct^3 +$ etc., as employed by Lüdin and other observers, cannot be found to represent the variation of the specific heat of water over the range 0° to 100° C. in a convenient and satisfactory manner. For this reason the results of the continuous electric method, when first published,* were represented by two or three very simple formulæ, covering different ranges of temperature. These have now been combined into a single continuous formula of a slightly different type, which is, in many respects, more convenient and accurate. The same formula also represents the most probable reduction of Regnault's results between 110° and 190° C., but may require modification over this part of the range when the continuous mixture method has been extended to higher temperatures. The formula for the specific heat s, at a temperature t, is as follows:—

$$s = 0{\cdot}98536 + 0{\cdot}504/(t+20) + 0{\cdot}0084(t/100) + 0{\cdot}0090(t/100)^2.$$

The terms in this formula are all small and positive, and can be calculated with sufficient accuracy for all purposes by the aid of a 10-inch slide rule, which is far from being the case if a formula of the Lüdin type is employed. The specific heat at 20° C. is taken as unity, and the scale of temperature t is that deduced from the platinum scale pt by the difference formula,†

$$t - pt = 1{\cdot}50\, t\, (t-100) \times 10^{-4},$$

as proposed at the British Association at Dover in 1899.

The corresponding formula for the variation of the total heat h, reckoned from 0° C. in terms of the same unit and temperature scale,‡ is

$$h - t = 1{\cdot}1605 \log_{10}(t+20)/20 - 1{\cdot}1464(t/100) + 0{\cdot}42(t/100)^2 + 0{\cdot}30(t/100)^3.$$

The unit at 20° C. is the most convenient to adopt in accurate work for many reasons. In particular, the difference $h-t$ is always small and positive, in this case, between 0° and 100° C.; whereas, if the unit at 15° C. is adopted, the values of $h-t$ are negative over half the range.

Tables of s, and of $h-t$, calculated from the above formulæ, are given in the paper for each degree from 0° to 200° C. The absolute value of the mechanical equivalent at 20° C. is 4·180 joules per gramme-degree C. within the possible limits of error of the absolute measurements. The value at any other temperature is 4·180 s.

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[*] 'B. A. Rep.,' 1899.

[†] Recent experiments by Holborn and Henning ('Ann. Phys.,' 1911, vol. 35, p. 761) appear to show that this formula gives a better approximation to the absolute scale than has hitherto been supposed.

[‡] Dieterici's latest results ('Ann. Phys.,' 1905, vol. 16, p. 593) for the mean specific heat agree to 1 in 1000 (his limit of accuracy) with this formula over the range 0° to 100° C. But his results for the actual specific heat at t exceed those of Regnault when reduced to the same unit by 3 per cent. at 200° C., a discrepancy which appears to require further investigation.